An efficient catalyst for the production of isobutanol and methanol from syngas. XI. K- and Pd-promoted Zn/Cr/Mn spinel (excess ZnO)

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A 2.25 wt% K- and 6.0 wt% Pd-promoted Zn/Cr/Mn spinel (excess ZnO) higher alcohol synthesis (HAS) catalyst has been tested for the production of isobutanol and methanol at 440 °C and 1500 psig. An isobutanol production rate of 179 $\mathrm{g\,kg^{-1}\,h^{-1}}$, a methanol-to-isobutanol mole ratio of 1.3 and a total alcohol rate of 304 $\mathrm{g\,kg^{-1}\,h^{-1}}$ are attained. This ratio is slightly higher than the desired value of 1.0 for MTBE production. These results are superior to others presented in the literature thus far. Surface characterization data indicate that the near-surface region of the catalyst consists primarily of ZnO and K. Pretreating the catalyst in a reductive environment similar to that given to the catalyst before reaction tests, causes an enrichment of the K promoter at the surface. The product stream composition does not significantly change during five days of testing.

Keywords: higher alcohol synthesis, Cs- and Pd-promoted Zn/Cr/Mn spinel catalysts, isobutanol, methanol, synthesis gas

1. Introduction

The production of isobutanol and methanol from a syngas (CO and H_2) feedstream has received considerable attention in recent years. This research stems from the use of these two alcohol components directly as gasoline additives or in the downstream synthesis of methyl tertiary-butyl ether (MTBE), a fuel additive typically found in quantities of up to 3–5 wt% in the gasoline used today. MTBE is currently produced using C_4 petroleum feedstocks, but the development of a catalytic reactor system which produces an equimolar mixture of isobutanol and methanol with high selectivity from syngas, a coal-derived product, would lessen this dependence on petroleum. Recently, MTBE leakage from storage tanks has raised enviromental concerns so the direct blending of alcohols may be more important in the future.

Types of higher alcohol synthesis (HAS) catalysts include modified Fischer–Tropsch and methanol synthesis catalysts. The use of modified high-temperature, high-pressure, methanol synthesis catalysts results in the highest isobutanol-to-methanol mole ratios [1] with a ratio of 1.0, which is ideal for MTBE synthesis. These types of catalysts typically are composed of a Zn/Cr spinel structure which is promoted with Cs or K [1–6], and the addition of Cs usually results in better catalysts. Surface characterization data obtained from several HAS catalysts indicate that the near-surface regions of these catalysts primarily consist of ZnO [5–8] and not a Zn/Cr spinel. The Zn/Cr spinel structures are detected using X-ray diffraction (XRD), which probes bulk crystalline phases of the powder samples. These findings led to the study of HAS over a ZnO powder which simply was purchased from Aldrich Chemical Co. and promoted with K [9]. Although a low isobutanol production rate is obtained, the BET surface area of this catalyst is quite low compared to the Zn/Cr spinel based catalysts (approximately 0.2 : 1). On a surface-area basis, the 1 wt%, K-promoted ZnO powder is superior to all other catalysts described in the literature with regard to isobutanol production rate. The addition of Pd to Zn/Cr HAS catalysts also results in improved isobutanol and total alcohol production rates compared to similar catalysts which do not contain Pd [10,11].

In this paper reaction data collected using a Zn/Cr/Mn spinel-based catalyst containing excess ZnO and promoted with 2.25 wt% K and 6.0 wt% Pd are presented and compared with data obtained from a similar catalyst not containing Mn. The results obtained are excellent compared to those from HAS catalysts tested previously. Surface characterization results obtained using X-ray photoelectron spectroscopy (XPS) and ion scattering spectroscopy (ISS) are also shown.

2. Experimental

The Zn/Cr catalyst support material was prepared by flowing solutions containing a 4 : 1 molar ratio of $KOH:K_2CO_3$ and a mixture of 4 : 1 : 1 Zn : Cr : Mn nitrates dissolved in deionized water into approximately 1 l of deionized water at room temperature. The flows of

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each of the above streams were adjusted to maintain a pH of 10. The solution containing the coprecipitated product was heated to 70 °C and stirred for 3 h. The product was then filtered and washed three times with 3 l of deionized water. The remaining product was dried at 100 °C, ground to 40 mesh and analyzed to ensure that the bulk alkali metal levels were below 300 ppm. This material was then calcined in a tube furnace at 325 °C for 12 h. The catalyst was impregnated with 2.25 wt% K and 6.0 wt% Pd as promoters using K and Pd nitrates and the incipient wetness method. The resulting catalyst has a BET surface area of about 80 m^2/g.

The reactor consisted of a $1/4$ inch copper-lined tube which eliminates products formed due to feedstream reactions with stainless-steel tube walls at elevated temperatures. Since Cu is an active component in low-temperature HAS catalysts, blank studies were performed to ensure that HAS did not occur over the Cu. Under the conditions used in this study, a synergistic effect between ZnO and the Cu would produce hydrocarbons and not alcohols. One gram of catalyst was mixed with 3 g of glass beads for dispersion and then placed into the reactor tubes. The tubes were placed in an air-fluidized sand bath for uniform heating. The pretreatment and feedstream gases were passed through a molecular-sieve-activated carbon trap to remove water and metal carbonyl contaminants before entering the reactor tube. The catalyst was calcined in air at 325 °C prior to use in order to ensure catalyst stability. The catalyst pretreatment consisted of heating the sample at 300 °C for 4 h in a 5% hydrogen-in-nitrogen mixture. The reaction was run using a $1:1$ $CO:H_2$ mixture at a space velocity of 12,000 at 440 °C and 1500 psig. The product stream was analyzed with a Varian 3700 gas chromatograph using both thermal conductivity and flame ionization detection methods [5,6]. The focus of this study is the production of isobutanol so components produced in small quantities are neglected.

The details of the characterization experiments have been published previously [5]. The fresh catalyst samples were pressed into an Al cup and inserted into the characterization system where XPS and ISS analyses were carried out with a double-pass cylindrical-mirror analyzer (PHI model 25-255AR). This sample was then exposed to 1×10^{-7} Torr of H_2 for 4 h at 325 °C and analyzed again without air exposure. The samples aged in the reactor for 5 days were exposed to air before analysis by XPS and ISS.

3. Results and discussion

Product stream compositions obtained from the 2.25 wt% K/6.0 wt% Pd/Zn/Cr/Mn for the spinel catalyst (catalyst A) at 1500 psig and 440 °C are given in table 1. For comparison the results obtained using a 3 wt% Cs/5.9 wt% Pd/Zn/Cr spinel containing excess ZnO (catalyst B) at 1000 psig and 440 °C [12] are also given in table 1. Under these conditions methanol is essentially at equilibrium. This is the second best catalyst identified in this study. There are two differences between these catalysts. The first is that catalyst A contains K as a promoter rather than Cs. For a given catalyst formulation, Cs always performs better. In this case a Cs-promoted catalyst prepared with this formulation has not been tested. It may perform better than the K-promoted catalyst described in this study. The second difference is that much of the Cr has been replaced by Mn in catalyst A. Since Mn is less acidic than the Cr, it may produce less hydrocarbons. Catalyst A produces 304 $g\,kg^{-1}\,h^{-1}$ of alcohols compared to 228 $g\,kg^{-1}\,h^{-1}$ for catalyst B, and the methanol-to-isobutanol mole ratio is 1.3 compared to 0.44 for catalyst B. The total alcohol rate and isobutanol production rate is approaching that required to make this process economically viable (approximately 400 $g\,kg^{-1}\,h^{-1}$ at a methanol-to-isobutanol ratio of 1.0 under current economic conditions). Although the se-

Table 1
Product stream compositions obtained using a 2.25 wt% K/6.0 wt% Pd/Zn/Cr/Mn spinel catalyst (catalyst A), a 3 wt% Cs/5.9 wt% Pd-promoted Zn/Cr spinel containing excess ZnO (catalyst B) and a 3 wt% K/5.9 wt% Pd-promoted Zn/Cr spinel catalyst containing excess ZnO (catalyst C). The numbers in this table are an average over a 5 day operating period. The reaction was run using a $1:1$ $CO:H_2$ mixture at a space velocity of 12,000.

	Catalyst		
	A	B	C
P (psig)	1500	1000	1500
T (°C)	440	440	400
Selectivity to total alcohols (%)	64	71	57 (49)[a]
Total alcohol rate ($g\,kg^{-1}\,h^{-1}$)	304	228	221 (217)
Methanol rate ($g\,kg^{-1}\,h^{-1}$)	99	32	54 (69)
Ethanol rate ($g\,kg^{-1}\,h^{-1}$)	0.0	0.0	8 (11)
Isopropanol rate ($g\,kg^{-1}\,h^{-1}$)	0.0	4	5 (3)
n-propanol rate ($g\,kg^{-1}\,h^{-1}$)	27	23	18 (19)
Isobutanol rate ($g\,kg^{-1}\,h^{-1}$)	179	170	136 (116)
MeOH/i-ButOH mole ratio	1.3	0.44	0.92 (1.67)
Hydrocarbon rate ($g\,kg^{-1}\,h^{-1}$)	94	49	111 (157)
Conversion (%)	28	19	23 (21)

[a] The values in parentheses were estimated by linear interpolation of the data presented in [23].

lectivity to total alcohols is lower for catalyst A (64 versus 71%), the reactant conversion rate is much larger (28 versus 19%). Therefore, the hydrocarbon production rate of 94 $\mathrm{g\,kg^{-1}\,h^{-1}}$ for catalyst A is almost double that for catalyst B. The hydrocarbons consist mostly of methane, some ethane and propane but more C_4 than C_2 and C_3. These data indicate that the primary function of the Mn is not to increase the selectivity toward alcohols but to increase the overall catalyst activity. This is consistent with the results of a previous study [9] in which K-promoted ZnO powder was tested for HAS activity. On a surface-area basis, this is the most active catalyst examined for HAS thus far. This result and those presented in this study indicate that the presence of Cr lowers the activity of these catalysts toward HAS.

Beretta et al. [4a,b] have reported isobutanol production rates of 74.1 $\mathrm{g\,kg^{-1}\,h^{-1}}$ using a Cs-promoted Zn/Cr catalyst with a high methanol-to-isobutanol mole ratio of approximately 5.4. Tronconi et al. obtained an isobutanol production rate of 25.8 $\mathrm{g\,kg^{-1}\,h^{-1}}$ using a K-promoted Zn/Cr catalyst [13] and 18.9 $\mathrm{g\,kg^{-1}\,h^{-1}}$ using a Cs-promoted Zn/Cr catalyst [14] while Nunan and coworkers [15] have tested a Cs-promoted, low-temperature, low-pressure methanol synthesis catalyst (Cu/ZnO) and observed an isobutanol production rate of 48.6 $\mathrm{g\,kg^{-1}\,h^{-1}}$. A similar catalyst but supported on Al_2O_3 results in an even lower isobutanol production rate of 9.4 $\mathrm{g\,kg^{-1}\,h^{-1}}$ [16]. A separate study by Boz et al. [17] was performed using the alumina-supported samples, but promoted with K, and these authors observed catalyst deactivation within the first 10 h of reaction. No change in the product stream composition occurred during the experiments performed in the present study over a five-day test period. Stiles et al. [18] examined a Cu/Mn/Zn/Cr/K catalyst and obtained an isobutanol production rate of only 20.2 $\mathrm{g\,kg^{-1}\,h^{-1}}$ while in another study Campos-Martin et al. [7] obtained a value of 13.7 $\mathrm{g\,kg^{-1}\,h^{-1}}$ using a Cs-promoted Cu/Zn/Cr catalyst. Furthermore, other types of catalysts do not yield higher isobutanol production rates. An Fe-containing Cu/Mo catalyst yields a total alcohol production rate of 51.9 $\mathrm{g\,kg^{-1}\,h^{-1}}$ with 57% of the alcohol products composed of methanol [19]. A recent report by Apesteguia et al. [20] and related patents by this Exxon group [21] have shown that the use of a K/Cu/Mg/Ce sample catalyzes the synthesis of isobutanol and methanol at low temperatures, but again the isobutanol production rate is low with 7.16 $\mathrm{g\,kg^{-1}\,h^{-1}}$ formed over the best of the catalysts tested. Keim and Falter [11] have reportedly obtained excellent isobutanol synthesis rates, although Forzatti et al. [1] state that these values are similar to those obtained using their catalysts, which are listed in the discussion above [1,13,14]. As indicated from comparison of the values presented above and those shown in table 1, catalyst A described here performs better than any others described in the literature. Furthermore, the production rates presented here represent significant improvements over others obtained using the same reactor system under identical conditions [5,6,9,10].

Herman, Klier and coworkers [4c,d] have described a two-catalyst-bed system for producing mixtures of methanol and isobutanol. The first bed contains a Cs-promoted $Cu/ZnO/Cr_2O_3$ catalyst and operates at low temperatures compared to the second bed, which contains a Cs-promoted ZnO/Cr_2O_3 catalyst [4c] or the Cs-promoted $Cu/ZnO/Cr_2O_3$ catalyst [4d]. This latter two-bed system exhibits a high production rate of 202 $\mathrm{g\,kg\text{-}cat^{-1}\,h^{-1}}$ of isobutanol, but the methanol-to-isobutanol mole ratio is above 6. As the second-bed temperature is decreased, both the isobutanol and methanol yields are decreased as is the methanol-to-isobutanol mole ratio. Although two-bed catalyst systems are economically less desirable than a single reactor system, they may be optimal based on their performance. Further improvements in performance of two-catalyst-bed systems may be obtained using the more active catalyst described in this study.

In order to gain more insight into how the Mn alters the performance of HAS catalysts, the product stream composition obtained using a 3 wt% K- and 5.9 wt% Pd-promoted Zn/Cr spinel containing excess ZnO (catalyst C) is also given in table 1. This K loading is 0.75 wt% higher than that for catalyst A, but other than that the only difference is the presence of Mn in catalyst A. Catalyst C performs significantly better than a similar catalyst with a 1 wt% K loading [12]. This implies that a catalyst with a 2.25 wt% loading would not perform as well as catalyst C. Based on the data given in [9], estimates of the performance of a catalyst with a 2.25 wt% loading is shown in parentheses in table 1. These catalysts clearly perform worse than catalyst A in that they have lower selectivities to total alcohols, lower total alcohol rates and higher production rates of hydrocarbons. This improved performance is due to replacement of Cr with Mn.

XPS and ISS surface characterization techniques were both used in order to gain a better understanding of these catalysts. High-resolution XPS Pd 3d and Zn(LMM) spectra obtained from these catalysts are shown in figure 1. Spectra (a) and (b) were obtained from catalyst A before and after pretreatment, respectively. The Pd in the as-prepared sample consists of PdO_2, and during pretreatment a small amount is reduced to metallic Pd. The spectrum shown in figure 1(c) was obtained from a 5 wt% K- and 5.9 wt% Pd-promoted Zn/Cr spinel containing excess ZnO after pretreatment at 10^{-7} Torr in H_2 at 300 °C for 4 h. For this catalyst the PdO_2 peak is quite large relative to the Zn Auger features and a small metallic Pd feature also appears to be present. The relative size of an XPS feature depends both upon the amount present in the near-surface region and the manner in which this species is distributed throughout the region probed by XPS [22]. Since the amounts of Pd present in the near-surface regions of these catalysts are similar, the larger Pd feature in figure 1(c) indicates that the Pd is distributed differently in these catalysts. It is either closer to the surface and/or spread out more uni-

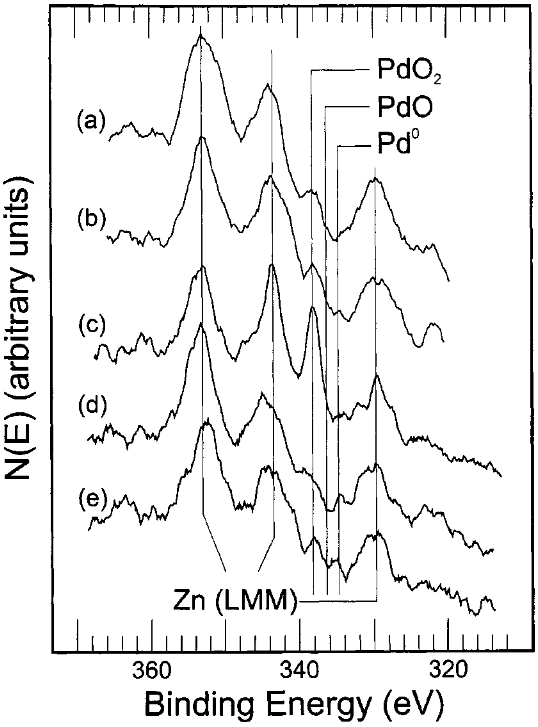

Figure 1. High-resolution XPS Pd 3d spectra obtained from catalyst A (a) before and (b) after pretreatment, (c) a 5 wt% K- and 5.9 wt% Pd-promoted Zn/Cr spinel with excess ZnO after reductive pretreatment and catalyst B (d) before and (e) after pretreatment.

formly across the surface. The spectra shown in figure 1 (d) and (e) were obtained from catalyst B before and after reductive pretreatment, respectively. These spectra are quite similar to those obtained from catalyst A except that a larger fraction of the Pd is present as metal.

The Zn(LMM) peak shapes also vary in figure 1. Shoulders can be observed which vary in a systematic manner with reductive pretreatment. This is not unexpected since Auger peak shapes and positions are usually more sensitive to chemical-state changes than the direct photoemission features because the Auger features involve three energy levels, while the direct photoemission features each involve one. However, relatively little has been done with regard to examining chemical-state effects on Zn Auger features so no attempt will be made here to interpret the Zn chemical-state changes based on these Auger spectra. These spectral changes are consistent with the fact that the Zn plays an important role in this catalytic process.

ISS is a powerful surface characterization technique for studying catalysts [22], which provides compositional information about the outermost atomic layer. This is important because catalytic reaction occurs at the outermost atomic layer. An ISS spectrum obtained from the as-prepared catalyst A is shown in figure 2(a). The signal-to-noise ratio of this spectrum is relatively low and few distinct features are apparent. This is typical of a surface that is highly oxidized. The features which are evident are due to K and Pd. Neither of these elements are prominent in the XPS data obtained from this sample. This seemingly contrary result is due to the differences in probing depths of these two techniques. Although ISS is sensitive only to the outermost atomic layer, XPS typically probes approximately 60 Å beneath the surface. Furthermore, the XPS signal contribution arising from the outermost layer is normally less than 10% of the total signal [22]. Therefore, the fractional monolayers observed using ISS may be below the detection limits in XPS for a given set of data collection parameters particularly if significant quantities of the same elements are not present in the subsurface region. The low, broad feature ranging from an E/E_0 of 0.20–0.40 is due to both C and O. These elements have very small ISS cross sections compared to the other elements present because their masses are relatively small [22]. The ISS spectrum obtained from the pretreated catalyst A (figure 2(b)) contains a large feature due to K at the outermost atomic layer of the sample, and features due to O, Cr, Zn and Pd are evident also. Cr and Mn cannot be distinguished in these ISS spectra since their masses are similar. Compared to spectrum (a), the features in spectrum (b) are much better defined and the signal-to-noise ratio is significantly increased indicating that the reductive treatment produces a more electrically conductive surface [22].

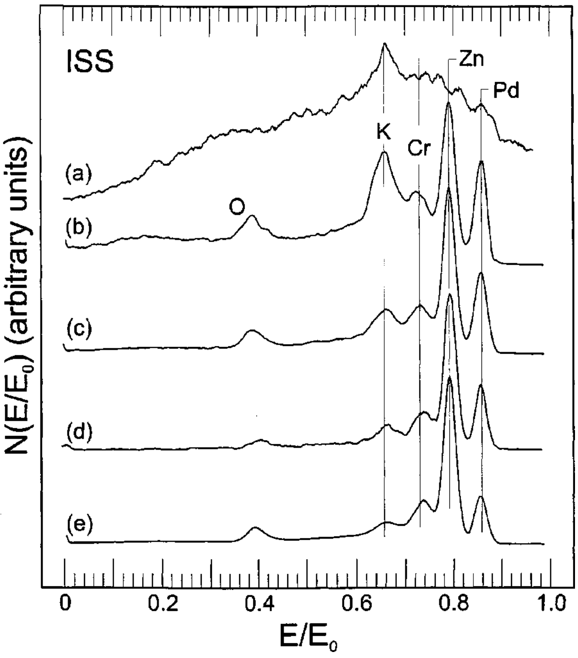

Figure 2. ISS spectra obtained from catalyst A after (a) insertion into the UHV surface characterization chamber, (b) pretreatment in 1×10^{-7} Torr of H_2 at 325 °C for 4 h and sputtering with 1 keV He^+ for (c) 5, (d) 15 and (e) 38 min.

A compositional depth profile was obtained from the pretreated catalyst by sputtering the sample with He^+ and taking ISS spectra at various intervals. The spectrum shown in figure 2(c) was obtained after sputtering catalyst A with 1 keV He^+ for 5 min. The amount of K at the surface is significantly reduced relative to the other components indicating that the surface is enriched in this promoter. The

Pd signal is also smaller relative to the Zn feature indicating that the Pd preferentially resides at or near the surface as well. Continued sputtering results in further decreases in the Pd and K signal intensities, as shown in figure 2 (d) and (e), which were obtained after 15 and 38 min of sputtering with 1 keV He^+, respectively. The Zn : Cr ratio remains relatively constant indicating that they are uniformly distributed throughout the depth examined. The O signal also does not change significantly, as expected. Corresponding ISS spectra have been obtained from catalyst B, and these are shown in figure 11 of [23]. In this case the spectra are not as revealing because the Pd and Cs features overlap each other. The most significant difference is that after reduction a very small Zn feature is barely discernible compared to the large Pd/Cs feature whereas the Zn feature predominates for the pretreated catalyst A surface. With ion sputtering the Pd/Cs feature is reduced in intensity relative to the Zn and Cr features, as expected. Furthermore, a small amount of Na contaminant is also present at the surface before and after pretreatment, which becomes more prominent with sputtering.

4. Summary

A 2.25 wt% Cs/6.0 wt% Pd/Zn/Cr/Mn catalyst which contains excess ZnO was tested for HAS. The reaction data indicate that this catalyst is highly efficient for the production of isobutanol with a production rate of 179 $g\,kg^{-1}\,h^{-1}$ at 440 °C and 1500 psig and a total alcohol production rate of 304 $g\,kg^{-1}\,h^{-1}$. These values are greater than any previously reported values in the literature for an HAS catalyst. Furthermore, a methanol-to-isobutanol ratio of 1.3 is attained at these operating conditions, which is close to the desired value of 1.0 for downstream production of MTBE. The function of the Mn is to increase the catalyst activity, increase the selectivity to alcohols by decreasing the hydrocarbon by-product rate and increase the isobutanol production rate. Reaction data obtained in this and previous related studies indicate that the presence of Cr is detrimental for HAS. HAS catalysts should be examined which contain no Cr.

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